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The thermoluminescence curves are analyzed for KCl crystals and an energy diagram is proposed to correlate the thermoluminescent spectra with optical absorption measurements. An attempt to analyze the thermoluminescence curves for KBr and KCl crystals indicates a monomolecular process for the KBr and a multimolecular process for the KCl crystals.

THERMOLUMINESCENCE AND OPTICAL ABSORPTION STUDIES OF HIGHLY PURE KCl CRYSTALS

by

Smita Pralhad Vaidya

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Approved by

Thesis Adviser

APPROVAL PAGE

This thesis has been approved by the following committee of the Faculty of the Graduate School at The University of North Carolina at Greensboro.

Thesis Adviser G T Hogesett

Oral Examination Committee Members Richard T. Whitlock

Henry L. Anderson

July 29, 1971
Date of Examination

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INTRODUCTION

The existence of colored specimens of normally colorless minerals has been known for much longer than a century and has created excitement among mineralogists, physicists and chemists. Since early 1800, researchers have studied this coloration phenomenon through bleaching experiments, thermoluminescence, and reproduction of the coloration by electric sparks, ultraviolet light, high energy corpuscular radiation and chemical means. The discovery of ionizing radiation (X-rays and radioactivity) and the observation that this coloration could be reproduced by exposure to this radiation enhanced the interest which led to a more systematic and continuous study. Pohl[1] did the most fundamental study of coloration on alkali halides and gave the name "color centers" to the "special electronic configuration in solids that gives rise to optical absorption in a normally transparent spectral region."[2] The phenomenon involved in the coloration was realized to be important if one is to understand the electronic processes in solids.

The major studies in the field of color centers have been done on alkali halides because they are typical ionic compounds and their properties are well known. Most alkali halides have interlocking face centered cubic

structure in which each alkali metal ion is surrounded by six nearest-neighbor halogen ions and vice versa. The alkali halides can be obtained in a reasonable degree of purity. "These salts are transparent from the far ultraviolet into far infrared, and therefore a very broad spectral region in which changes in optical absorption can easily be detected."[3]

There are several kinds of the color centers due to different electronic structures in the crystals. Since the structural imperfection highly influences the physical properties of solids, it is very clear that imperfections were involved in the production and the constitution of the color centers. In 1937 de Boer[4] proposed a model for one of the color centers in alkali halides which is the simplest color center; called the "F centers" the name comes from the German word for color Farbe. An F center consists of an electron trapped at the position of missing halogen ion (halogen ion vacancy). Figure 2 shows a schematic diagram of an F center. This model has survived the tests of further theoretical and experimental investigation and its correctness is firmly established. Seitz[5] proposed models for other color centers which involved electrons or electron deficiencies (positive holes) trapped at aggregates of positive or negative ion vacancies.

There are various ways[6,7] to produce color centers. The most advantageous way for the present study was by

Figure 1

A Schematic Diagram of the F Center

X-irradiation because it can generate free electrons and holes and hence keeps the sample electrically neutral; and normally it also does not change the stoichiometry of the crystal.

The amount of coloration received by the material is a function of X-ray exposure time, temperature at which this radiation is performed and the purity of the crystal.

The techniques used in studying the properties of color centers are as varied as are the interests of the people doing the research. The most common types of measurements are those dealing with optical and luminescence properties of crystals containing color centers.

Optical absorption[8,9] measurements are confined usually to wavelengths 1850Å to 30000Å, since the most commercial monochromators are confined to this wavelength region.

In the optical absorption measurement, the absorption of a crystal that contains color centers is compared with a crystal that does not contain color centers. This comparison is made as a function of wavelength. If I_o is the intensity of light transmitted by the uncolored crystal, the absorption may be described by the optical density (O.D.), where

$$O.D. = \log_{10}(I_o/I)$$

This definition assumes that the incident light is of

constant intensity and no correction is necessary for the reflection losses at the surfaces. The optical density is directly proportional to the number of absorbing centers per cm^2 of the sample and is independent of the distribution of these centers along the direction of the light path. If the concentration of the color centers does not vary with the depth, the number of centers per cm^3 can be calculated from the absorption constant α. (See Smakula's equation in the "Theory" chapter.)

$$\alpha = \frac{\ln(I_o/I)}{x} = \frac{2.303(O.D.)}{x}$$

where x is the sample thickness in cm.

A photon that is absorbed by a color center will excite it and the center may lose this energy by the emission of a light quantum, a process known as luminescence.[10,11,12] The study of luminescence usually deals with the measurement of the excitation spectrum and emission spectrum.

The important information about color centers can be obtained by observing the changes when the crystal is gradually heated from some low temperature to higher temperature. As the temperature is raised, electrons and holes try to escape from their traps at an increasing rate. The freed charges can be recombined with each other or with other defects and give out luminescence by

recombination. The resulting "thermoluminescence"[13,14] or "glow" reaches to a maximum and then goes to zero as the supply of trapped holes or electrons is exhausted. The curve of the thermoluminescence light intensity vs. temperature is called the "glow curve." It may contain one or more glow peaks depending if there are one or several kinds of traps.

Trapped electrons and trapped hole centers formed by such means as x irradiation can be destroyed by illuminating it with the light of appropriate wavelength. This process is called "Optical bleaching,"[15] which is readily understandable in view of the fact that an electron trapped in a chloride ion vacancy comprises a system of a bound electron analogous to the hydrogen atom. As such it has various excited states into which the electron can be excited thermally or by the absorption of light. With the absorption of sufficient energy, the electron can be completely freed from the defect. This process parallels ionization of hydrogen atom. If a freed electron encounters a trapped hole during its migration through the crystal, it can fall into the hole and annihilate it.

THEORY

If an optical absorption experiment is performed on an alkali halide crystal, after exposure to intense penetrating x-rays, the graph of optical density vs. wavelength exhibits many characteristic absorption bands. Figure 2 is a graph of optical density vs. wavelength for a KCl crystal.

It is proposed[23] that the M center is a pair of two adjacent F centers. R_1 and R_2 centers are not understood. V_2 and V_3 centers are complex hole centers, i.e. a hole trapped at the positive ion vacancies is a V center. The charge on a hole is equal and opposite to that on an electron. The hole centers are not well understood.

There are various models of the F center. One of the proposed models for an F center is given by Stockmann.[17] The vacancy in this model is replaced by a box and the quantum states of a particle in a box are written down.

Another model takes the view of the fact that an electron trapped by a positively charged defect comprises a system analogous to a hydrogen atom.

A third model is proposed by Landau that F centers are self trapped electrons or polarons.[18]

As a starting point, all models assume the de Boer[4] model of the F center, an electron trapped at a

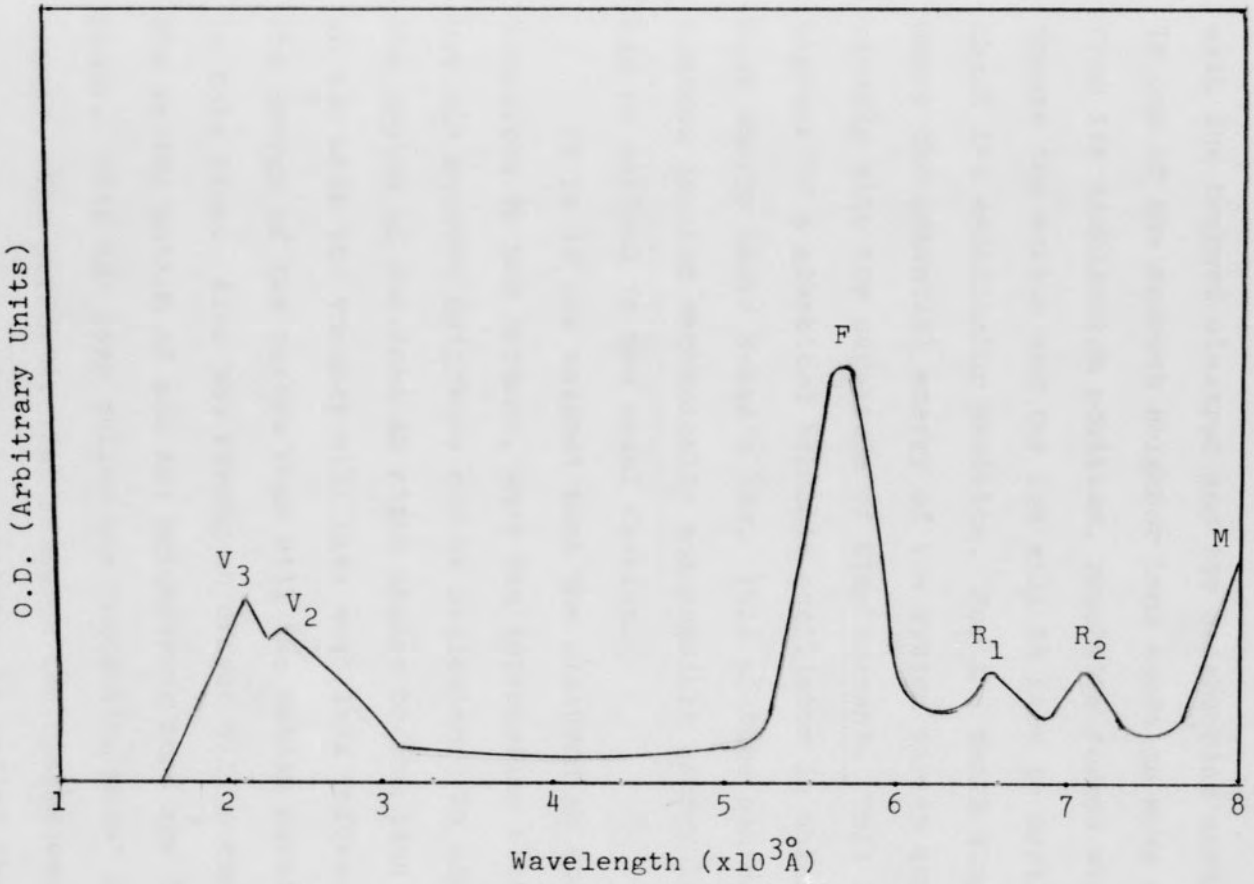

Figure 2

Formation of M, R_1, R_2, F, V_2 and V_3 Bands in KCl After Exposure to Intense X-Ray at Room Temperature

negative ion vacancy. The nuclei surrounding the vacancy assume positions that are determined by their interaction with the trapped electron and the neighboring nuclei. If one of the nearest neighbor ions tends to move away from its equilibrium position, repulsive forces will oppose the motion and the ion will be made to oscillate about its equilibrium position. For the small displacements the potential energy of the system varies quadratically with the magnitude of displacement. This is a picture of a classical harmonic oscillator in which potential energy obeys Hooke's law. This picture can be treated quantum mechanically and possible energy levels can be derived in the usual fashion.

If it is now assumed that the electron is strongly localized in the vacancy, then its interaction with all but six nearest neighbors can be neglected. In addition, the motion of the ions at right angles to the line joining an ion with the vacancy will have much less influence on the energy of the system than will the motion parallel to this line. Also the strongest effect will occur when the radial motion of all six neighboring ions are in phase. This has been called the "breathing mode" of the center. The parameter that measures the displacement of the ion from its equilibrium position is called the configuration coordinate. A plot of the total energy of a center as a function of its configuration coordinate is shown in Figure 3.

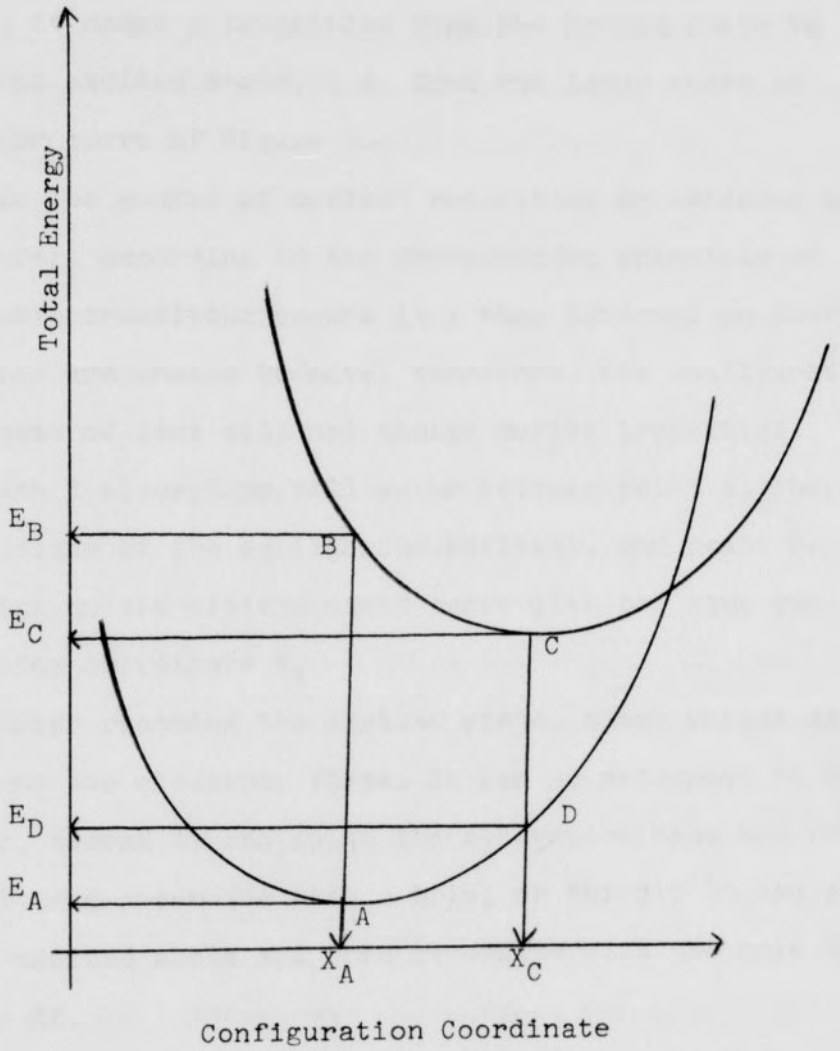

Figure 3
A Graph of the Total Energy vs. Configuration Coordinate

When the center is excited by the absorption of a photon, it makes a transition from the ground state to the first excited state, i.e. from the lower curve to the upper curve of Figure 3.

In the course of optical absorption or emission by the center, according to the Frank-Condon principle an electronic transition occurs in a time interval so short that ions are unable to move, therefore, the configuration coordinate of ions will not change during transition. In Figure 3 absorption will occur between point A, the ground state of the equilibrium position, and point B, the point on the excited state curve with the same configuration coordinate X_A.

After reaching the excited state, three things can happen to the electron; first, it can be retrapped in the vacancy, second it can go to the conduction band and from there it may recombine with a hole, or thirdly it can go to the excited state and then recombine with the hole and destroy it.

The process of retrapping can be understood in terms of Figure 3. In order for the electron to reach the point B on the excited state curve with the configuration coordinate X_A, a photon must have energy (E_B-E_A) to produce this excitation. The system at B is now in a state of excitation energy (E_B-E_C) in excess of the equilibrium energy E_C. The nuclei move to their new

equilibrium coordinate X_C with the loss of energy (E_B-E_C). This energy appears as heat, i.e. as lattice vibrations or phonons. From point C, the system can jump to D with the emission of a photon of energy (E_C-E_D). The center then loses an amount of energy (E_D-E_A) in the form of heat as it relaxes from D to A. Since the energy is lost as phonons it is obvious that (E_B-E_A) is greater than (E_C-E_D)(Stoke's shift).

The process of recombination of an electron with a hole involves two possibilities. Figure 4 is a schematic diagram of recombination of an electron with a hole.

From the ground state of the F center an electron may absorb energy of amount (E_E-E_G) and go to the excited state or it may absorb energy (E_C-E_G) and go to the conduction band. From the excited state or conduction band, the electron can recombine with the hole emitting a photon of energy (E_E-E_H) or (E_C-E_H).

The crystal can be shaken by supplying thermal energy and the electron may escape from the trap. If it encounters a hole during the course of its migration through the crystal, the electron will annihilate it.

A measurement of the height and the width of the F band can be used to determine the density of F centers in a crystal. The number of centers per cm^3, N_F is given by the relation known as Smakula's equation.[16] For KCl this relation takes the form

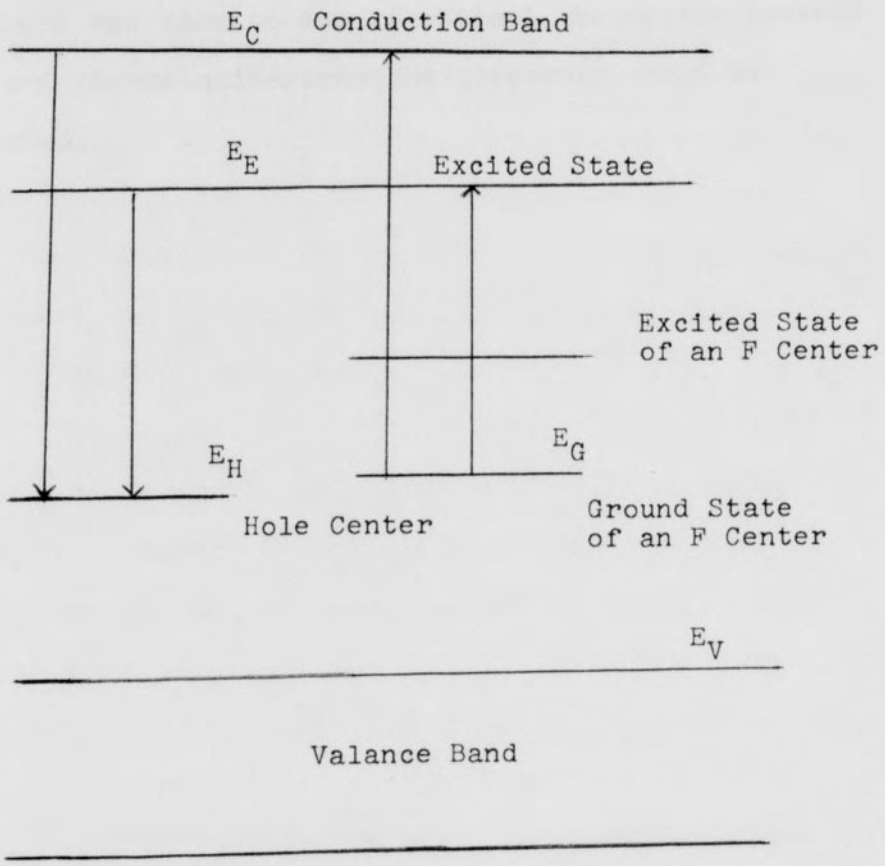

Figure 4

A Schematic Diagram of Recombination of an Electron with a Hole

$$N_F = 1.3 \times 10^{16} \alpha_{max} W_{1/2}$$

Where α_{max} is the maximum absorption constant in cm^{-1}

$W_{1/2}$ is the half width in electron volts.

Since highly pure KCl crystals became available, an attempt was made to see if optical absorption measurements and thermoluminescence measurements could be correlated.

EXPERIMENTAL SETUP

The X-ray machine used to color the crystals was a Phillips Electronic 120-101-00 Full Wave X-Ray Unit. It was operated at 35 kilovolts and 20 milliamps. There are three ports over which the crystal could be mounted. To keep the geometry of the coloration the same, the crystal was mounted on one port in the same position. The crystal was colored on one side only and a nickel filter about 0.25 mm thick was used to cut down the soft X-rays.

The experimental equipment used for the thermoluminescence studies consisted of a phototube with a high voltage supply, an electrometer, an x-y plotter for monitoring the output of the phototube, a soldering iron, a variac to adjust the heating rate, and a thermocouple to determine the temperature of the crystal. Figure 5 is a schematic diagram of the experimental equipment, showing necessary connections. A 6199 phototube was used for the experiment and a high voltage regulated direct current power supply was used to provide the operating voltage for the phototube. A Keithley 600A electrometer with sensitivity to 10^{-13} amps was employed for visual monitoring of the phototube current.

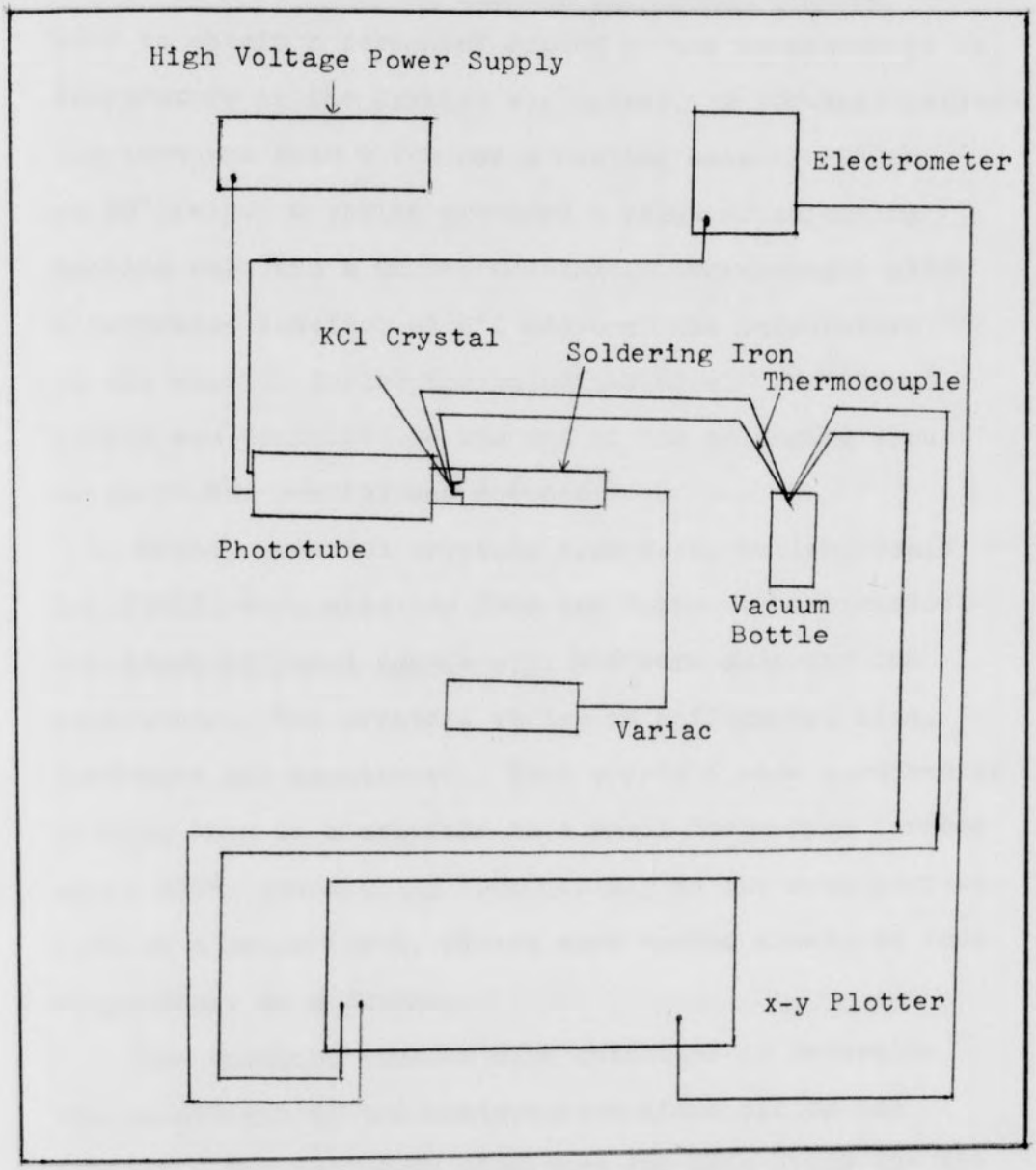

Figure 5

A Schematic Diagram of the Experimental Equipment
Showing the Necessary Connection

An x-y plotter from the Houston Instrument Company was used to obtain a permanent record of the luminescence vs. temperature as the crystal was heated. A 200-Watt soldering iron was used which has a heating rate of 22°C/min to 40°C/min. A variac provided a means of adjusting heating rate and a Copper Constantan thermocouple with a reference junction at 0°C measured the temperature of the crystal during thermoluminescence. The thermocouple was connected to the end of the soldering iron on which the crystal was mounted.

Highly pure KCl crystals from C. T. Butler, Boule No. 030766 were obtained from the Solid State Division, Oak Ridge National Laboratory, and were used for the experiment. The crystals varied in uniformity, size, thickness and smoothness. Some crystals were quenched by heating them in a crucible in a small Thermolyne furnace up to 400°C and cooling them quickly to the room temperature on a metal block, others were cooled slowly to room temperature in a furnace.

The spectral studies were conducted to determine the wavelength of the luminescence given off by the crystal. The equipment necessary for this study was the same as that required for the thermoluminescence studies with the addition of a monochromator equipped with a reversible micrometer drive which was placed between the

crystal and the phototube. The monochromator was a model F-11-20 ultraviolet infrared monochromator manufactured by Orion Optics Corporation. It has a calibrated wavelength range from 1900 to 15000Å and an adjustable slit width of zero to two millimeters. It has a quartz prism monochromator with inline configuration of the entrance and exit beam which makes possible installation into the optical path without disturbing its direction. The reversible micrometer drive was used to sweep the spectrum at a constant rate through the desired wavelength range. Because the addition of the monochromator moved the crystal further from the phototube thereby reducing the intensity of the thermoluminescence picked up by the phototube, and because the narrow slit further reduced the solid angle, the dark current of the phototube had to be greatly reduced for any thermoluminescence effect to be seen. This reduction was accomplished by packing the phototube with dry ice.

A Perkin Elmer Double Beam Spectrophotometer model no. 124 was used for the optical absorption measurements. The uncolored and the colored crystals were mounted on a stand and the sweep of the spectrophotometer ranged from 8000A° to 1800A°. The output of the sweep was recorded on a chart recorder.

For the optical bleaching measurements, a high intensity monochromator model no. 33-86-07 from Bausch

and Lomb Company was used. It bleached the crystal with the light of wavelength 5600Å.

PROCEDURE

The procedure of the thermoluminescence studies consisted of mounting the crystal on the soldering iron, X-raying it to create F centers, positioning the soldering iron close to the phototube with the more intensely colored side facing the phototube, sealing out the stray background light, heating the crystal while recording temperature and luminescence intensity, and then allowing the crystal to cool back to room temperature after the luminescence returned to zero.

For the spectral studies the procedure was the same. The dark current of the phototube which was normally around 6×10^{-9} amp was reduced to about 10^{-12} amp range by packing with the dry ice round the tube. When the temperature attained the proper value for a luminescence peak, the micrometer drive was switched on and a spectral sweep of wavelengths was made, usually from 3000 to 8000A°.

For the optical absorption measurement, the colored and uncolored crystals were mounted on a stand in front of a light source. The light of the wavelength 8000 to 1800A° was used and the absorption vs. wavelength curves were recorded.

ANALYSIS OF DATA

The first thermoluminescence studies were conducted on highly pure KCl crystals from Oak Ridge National Laboratory. An attempt was made to reproduce the two thermoluminescence peaks obtained by Jain and Mehendru. Their conclusion was "that in undeformed KCl crystals, X irradiated at room temperature, there are two thermoluminescence peaks characteristic of the pure KCl crystal. These peaks are at 135 and 190°C respectively, for the heating rate 40°C/min, and at 93 and 165°C for the heating rate 5°C/min."[19] A heating rate of 22°C/min was used. The crystals were exposed to X-ray intensity of 35 kilovolts and 20 milliamps for varying periods of time, ranging from 4 hours to 24 hours. In each case a sharp peak around 160°C and two shoulder peaks at 90°C and 220°C were obtained. The shoulder at 90°C was understood to be due to a divalent impurity in the crystal. This peak was removed by applying either of the two techniques; namely optical bleaching and heat treatment. The heat treatment technique is used to remove the unwanted thermoluminescent peaks from the crystal. The experimental setup is the same as that for the thermoluminescence. The crystal is heated up to desired temperature and then it is allowed to cool to room temperature. The shoulder at 220°C was understood to be a stress in the

crystal because bleaching with F light did not affect it. It was removed by heating the crystal for 24 hours at 400°C and cooling it slowly in the furnace to room temperature.

Figure 6 shows the thermoluminescence curves before quenching and optical bleaching.

Figure 7 shows the thermoluminescence curve after optical bleaching.

Figure 8 shows the thermoluminescence curve after heat treatment and quenching.

A spectral study was done on the crystal to determine the emission wavelengths of the glow curve. Table 1 shows the observed values of thermoluminescent spectra.

Table 2 shows the result of optical absorption measurement.

Table 3 shows the proposed values[20] of optical absorption measurements.

At room temperature the energy gap for KCl crystal is 7.70 eV[21] and the top level of an excited state of the F center is 0.15 eV[22] below the conduction band. The expected values of the thermoluminescent spectra can be calculated from the known value of the energy gap and Table 3 (see the explanation for Figure 10 below). Table 4 shows the computed values of thermoluminescent spectra.

Table 5 shows the percentage difference between the observed and the expected values of the thermoluminescent energy spectra.

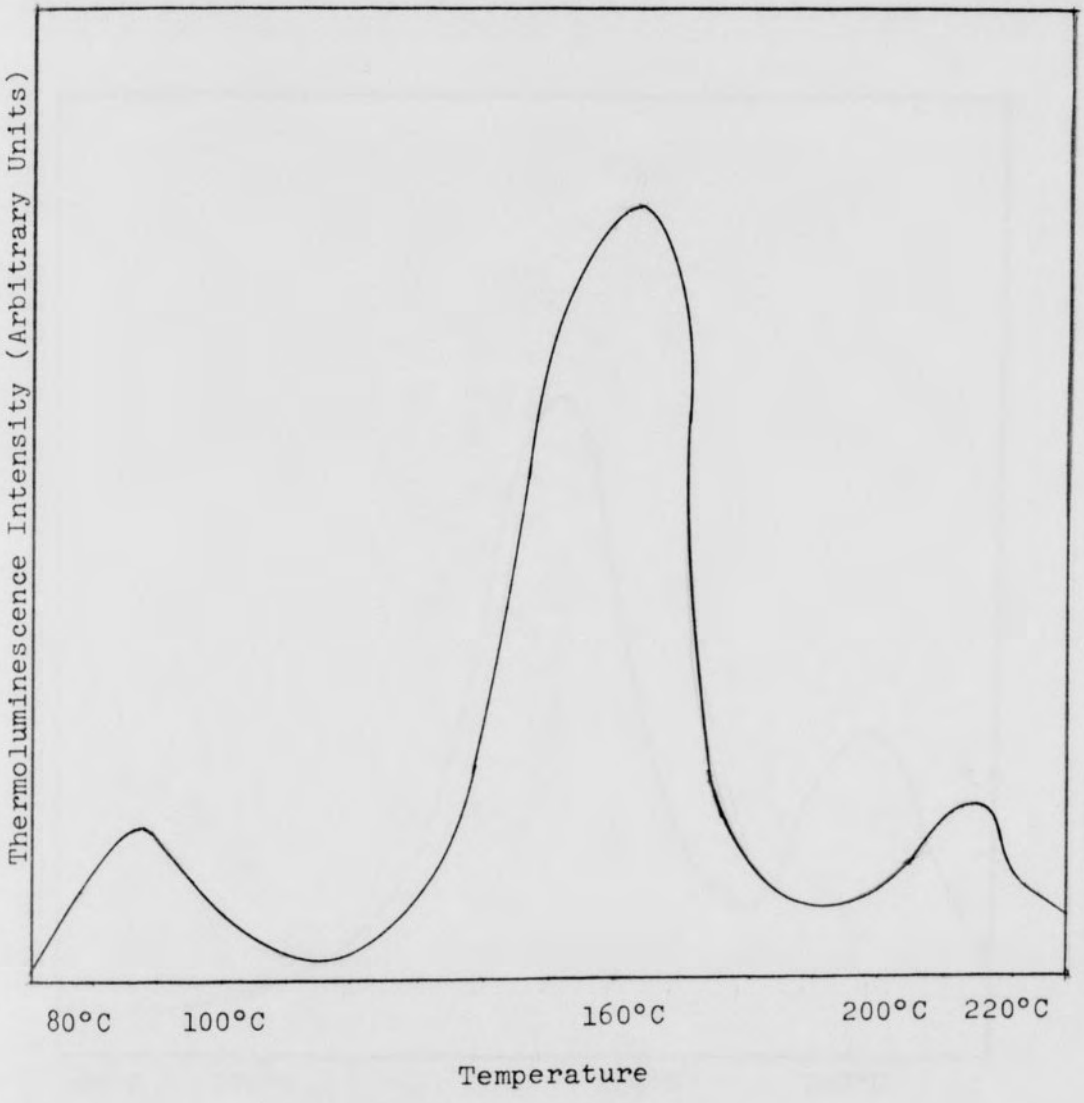

Figure 6

The Thermoluminescence Curve Before Quenching and Optical Bleaching

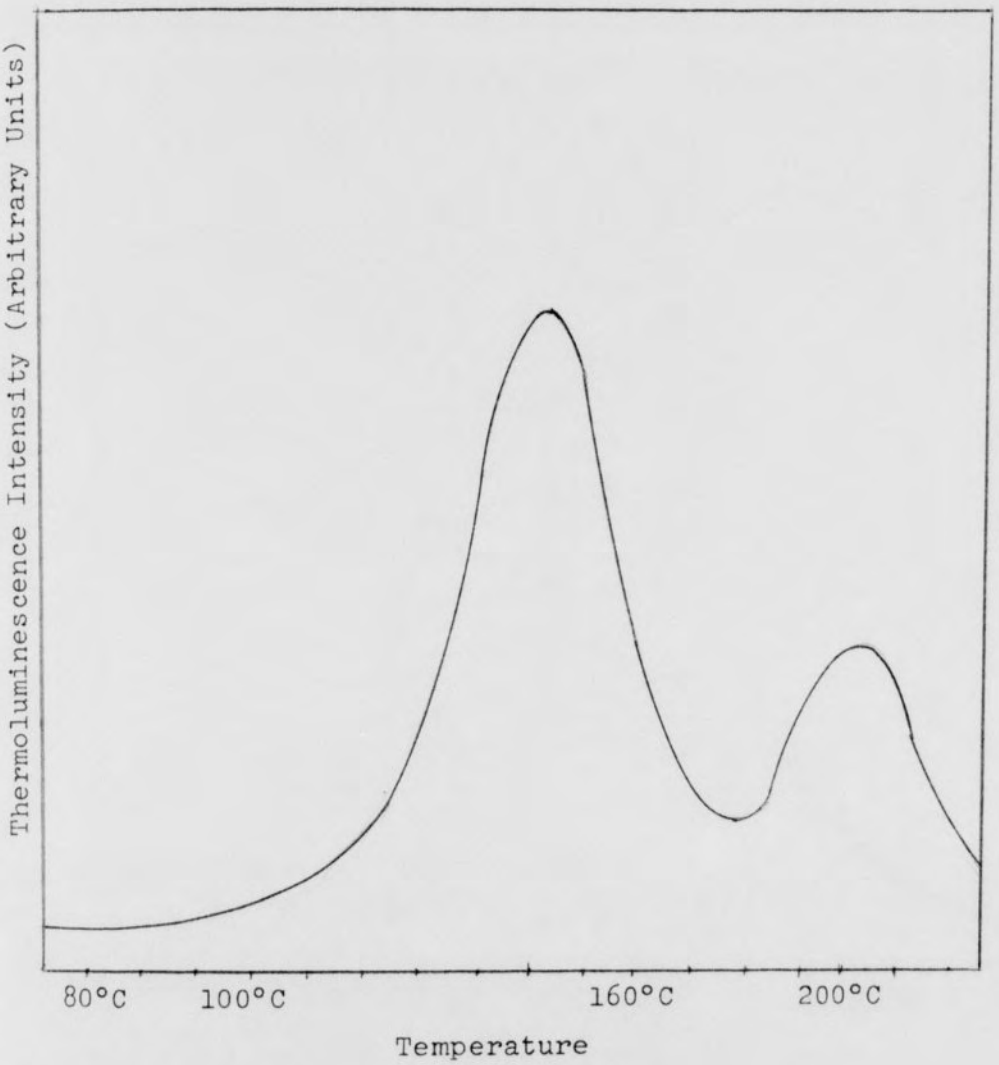

Figure 7

The Thermoluminescence Curve After Optical Bleaching

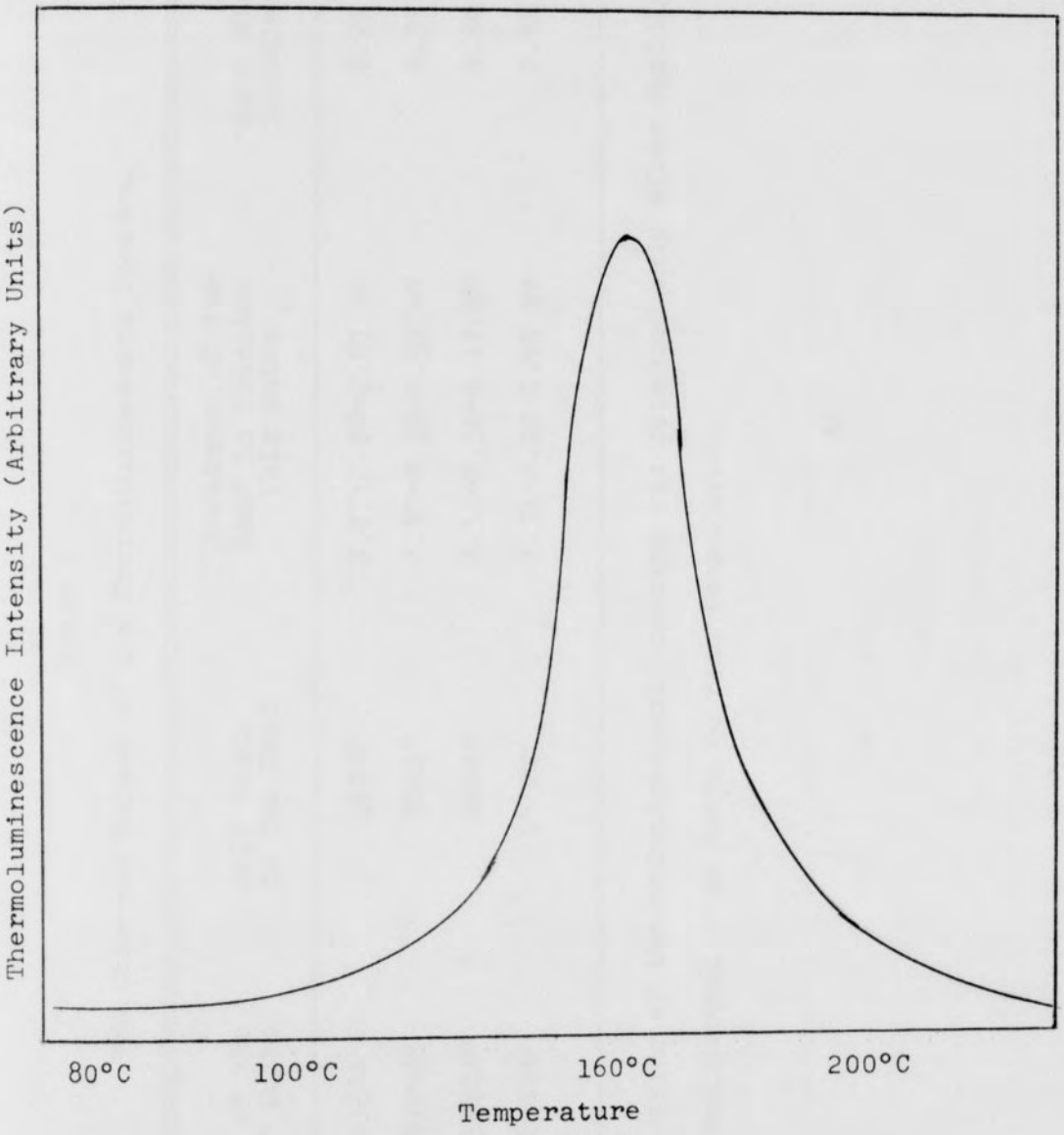

Figure 8

The Thermoluminescence Curve After Heat Treatment and Quenching

Table 1

The Observed Values of the Thermoluminescent Spectra

Broadness of the Band in A° Units	Half Width of the Band	Broadness of the Band in Electron Volt Units	Half Width in Electron Volts
4020→4200→4320A°	300A°	3.07→2.94→2.87 eV	0.20 eV
4320→4500→4900A°	580A°	2.87→2.75→2.53 eV	0.34 eV
4900→5350→5700A°	800A°	2.53→2.31→2.17 eV	0.36 eV
*5350→5700→6500A°	1150A°	2.31→2.17→1.90 eV	0.41 eV

*This value of thermoluminescent spectra was observed only after rapidly quenching the crystal from 700°C to room temperature.

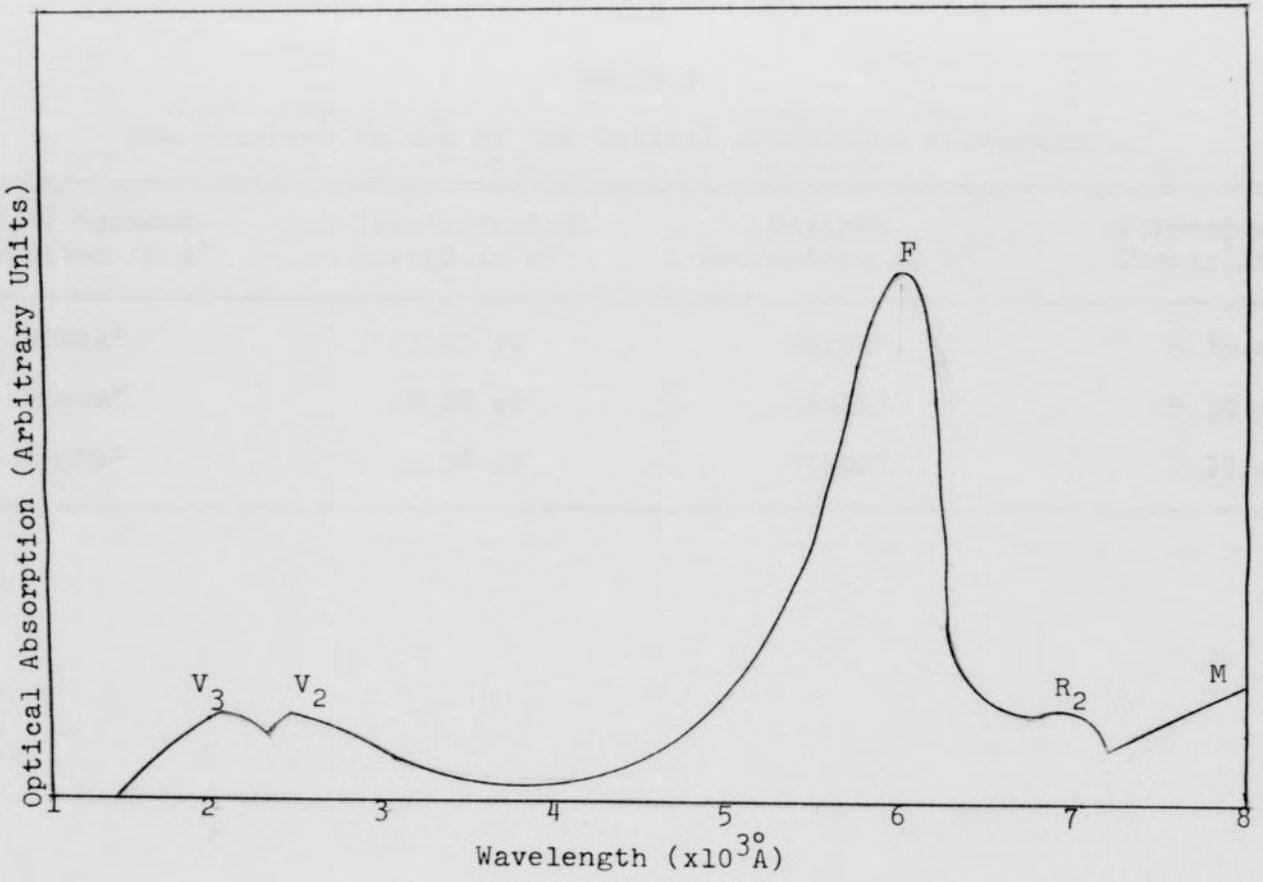

Figure 9

Optical Absorption Curve

Table 2

The Observed Values of the Optical Absorption Measurements

10% of Maximum Absorption in A°	Corresponding Energy in eV	Maximum Absorption in A°	Corresponding Energy in eV
2290A°	5.40 eV	2120A°	5.85 eV
2600A°	4.76 eV	230A°	5.39 eV
6330A°	1.96 eV	5550A°	2.23 eV

Table 3

The Proposed Values of Optical Absorption Measurements

10% of Maximum Absorption in A° Unit	Corresponding Energy in eV	Maximum Absorption in A° Unit	Corresponding Energy in eV
2310A°	5.37 eV	2120A°	5.85 eV
2600A°	4.76 eV	2300A°	5.39 eV
--	--	5600A°	2.21 eV

Table 4

The Expected Values of the Thermoluminescent Spectra

Maximum Luminescence in A° Unit	Corresponding Energy in eV
4217A°	2.94 eV
4440A°	2.79 eV
5380A°	2.33 eV
5700A°	2.18 eV

Table 5

The Percentage Difference Between the Observed and the Expected Values of the Thermoluminescent Spectra

Observed Values of the Thermoluminescent Spectra	Expected Values of the Thermoluminescent Spectra	% Difference
2.95 eV	2.94 eV	0.3%
2.75 eV	2.79 eV	1.0%
2.18 eV	2.18 eV	0.0%
2.32 eV	2.33 eV	0.4%

Figure 10 shows the quantitative picture of thermoluminescent spectra and optical absorption measurement.

Explanation of Figure 10

The energy gap for KCl crystal at room temperature is 7.70 eV; i.e. the "distance" between the valance band and the conduction band is 7.70 eV.

The optical absorption measurements show that there is a strong absorption at 5550Å. At that wavelength, the F center gets excited and as a result the electron goes to the excited state. The absorption at 2600Å is just enough to pump an electron from the valance band to the V_2 center. That absorption determines the "height" of the V_2 center from the top level of the valance band. At 2300Å the absorption for the V_2 center becomes the maximum. This absorption is proposed to be due to an electron 0.63 eV below the top level of the valance band. In the thermoluminescence experiment, the electron goes to either the conduction band or to the excited state. If it recombines with V_2 center, then the energy required for recombination must be either 2.94 eV or 2.79 eV. Therefore the light that has been given off because of this recombination must have the wavelength either 4217Å or 4440Å. The similar explanation can be given for the V_3 center.

An attempt was made to analyze the thermoluminescence curves for KBr and KCl crystals. Figure 11 and Figure 12

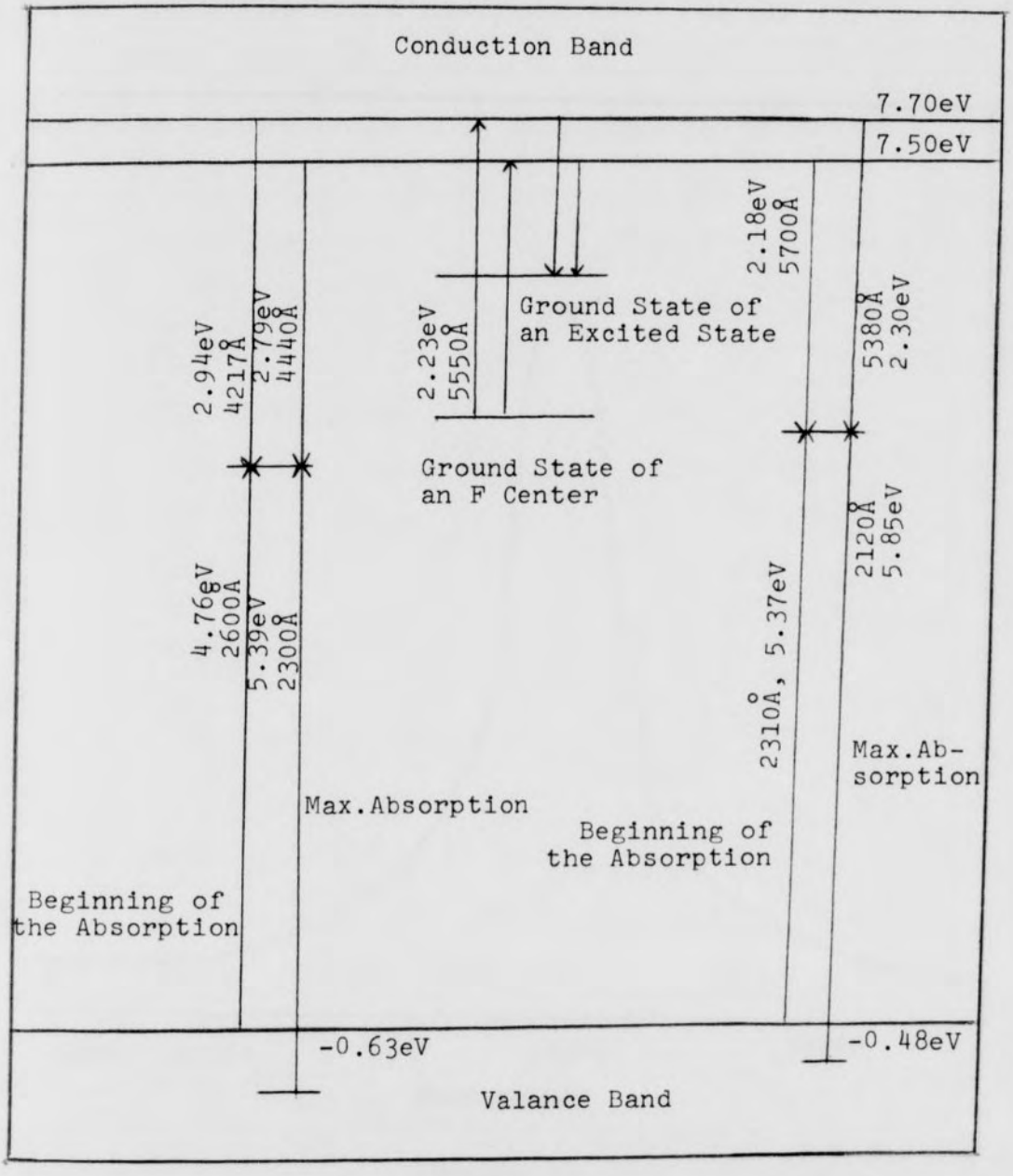

Figure 10

The Quantitative Picture of Thermoluminescent Spectra and Optical Absorption Measurement

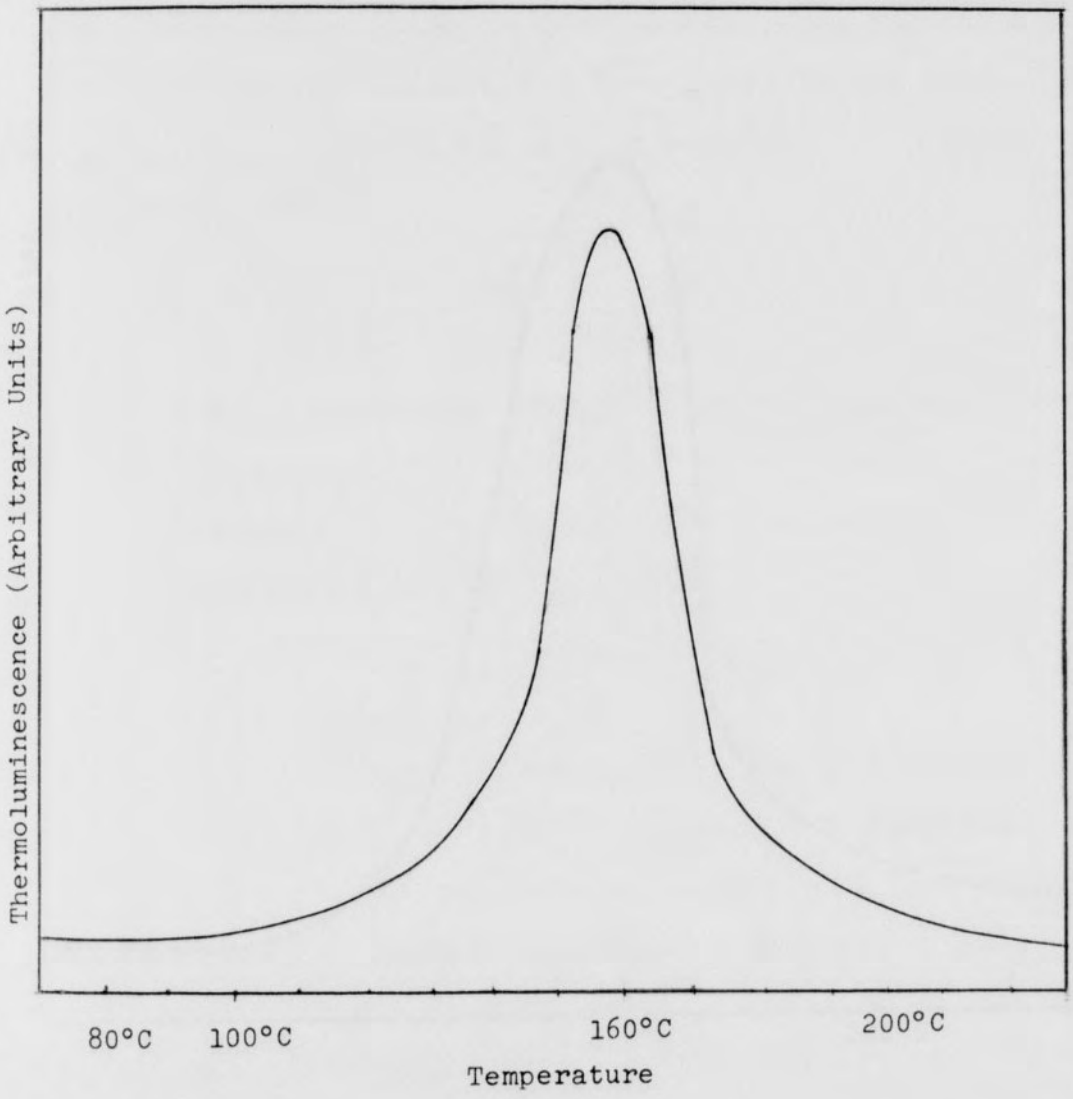

Figure 11

Thermoluminescence Curve for KBr Crystals

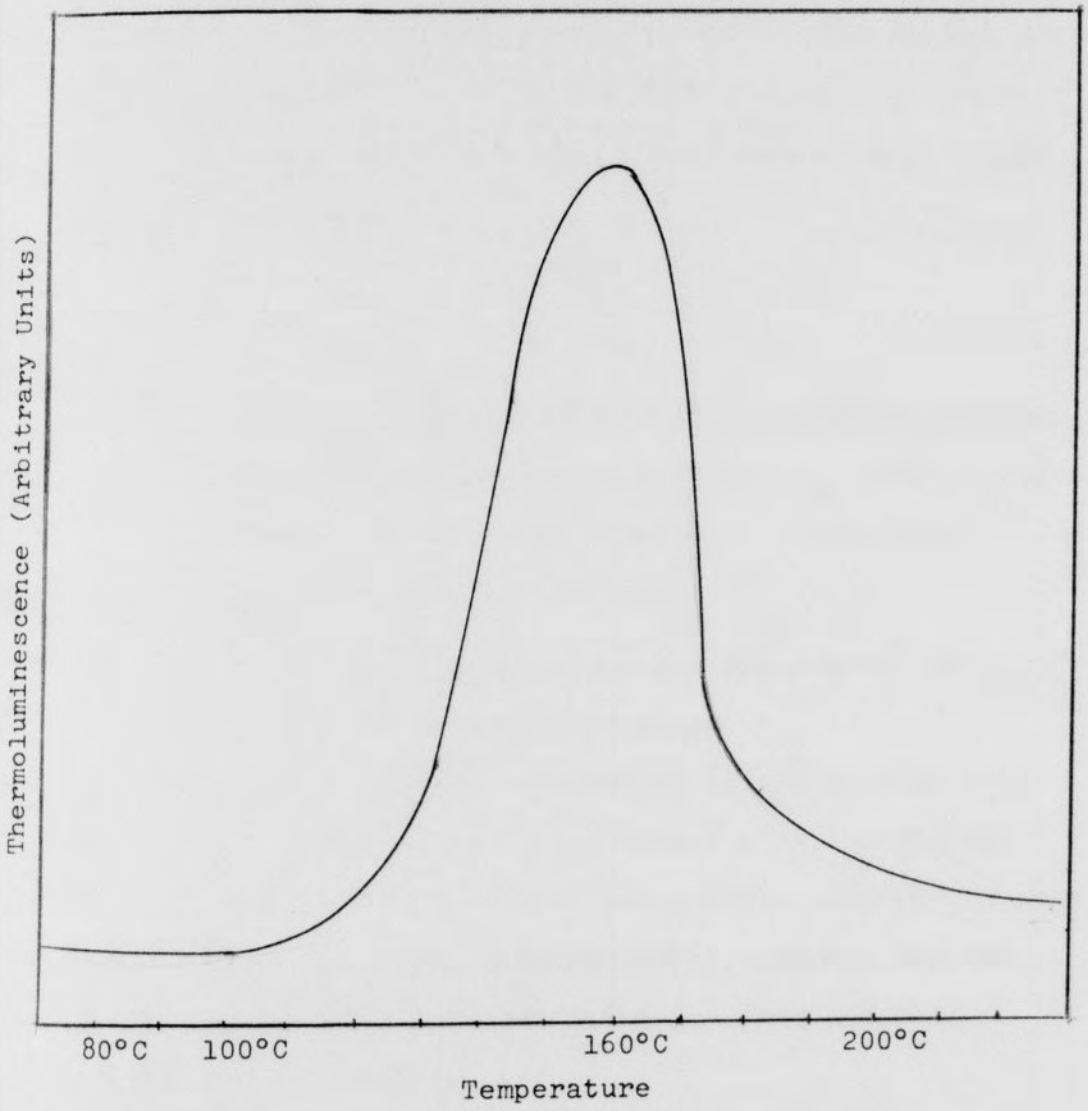

Figure 12

Thermoluminescence Curve for KCl Crystals

show the thermoluminescence curves for KBr and KCl crystals respectively. A single peak was obtained at 160°F for the KBr crystal while a peak at 165°C was obtained for the KCl crystal which was exposed to X irradiation for 12 hours. The following equation was used to calculate the q values for both crystals,

$$E = \frac{qkT_g^2}{\delta} ,$$

where

E is an activation energy K is a Boltzmann Constant, T_g is a peak temperature, $\delta = T_2 - T_g$; where T_2 is the temperature at half intensity on the high temperature side of the peak.

If $q < 1$ it is a monomolecular process but if $q > 1$ it is a multimolecular process.

The activation energy was determined by the initial rise method (see Appendix 1) and the values of q for KBr and KCl were found to be less than and greater than one respectively, which indicates a monomolecular process for KBr and a multimolecular process for KCl. (For detailed calculation see Appendix 2.)

SUMMARY AND CONCLUSION

Three peaks at temperature 90, 160 and 220°C were obtained from the thermoluminescence experiment. The peak at 90°C was understood to be due to a divalent impurity in the crystal which was removed by either heat treatment or by the optical bleaching. The peak at 160°C was considered to be due to the F center. This peak reduced in height after the exposure to the F light, and the optical absorption measurements showed the decrease in the height of the F band after F light bleaching. The peak at 220°C was understood to be a stress in the crystal because it was not affected by F light bleaching. It was removed by heating the crystal to 400°C for 24 hours and then allowing it to cool to room temperature in the furnace.

The optical absorption measurement showed that there was a strong absorption at 5550A° due to F center. The absorption was also observed at 2300A° and 2120A° due to V_2 and V_3 centers respectively.

The thermoluminescent spectra showed the evidence of emission of light at 2.79 eV and 2.30 eV due to the recombination of electrons with V_2 and V_3 centers.

The analysis of the thermoluminescence curve for the KBr crystal showed the indication of a monomolecular process while the same analysis for the KCl crystal showed the indication of a multimolecular process.

FOOTNOTES AND BIBLIOGRAPHY

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Appendix 1

The natural log of the thermoluminescence intensity varies directly as $\frac{10^3}{T}$; the constant of proportionality is $\frac{E}{k}$ where E is an activation energy and k is a Boltzmann Constant. If the natural log of the thermoluminescence intensity is plotted against $\frac{10^3}{T}$, then slope of the curve times k gives the activation energy. Figures 13 and 14 show the graphs of ln I vs. $10^3/T$ for KBr and KCl crystals respectively.

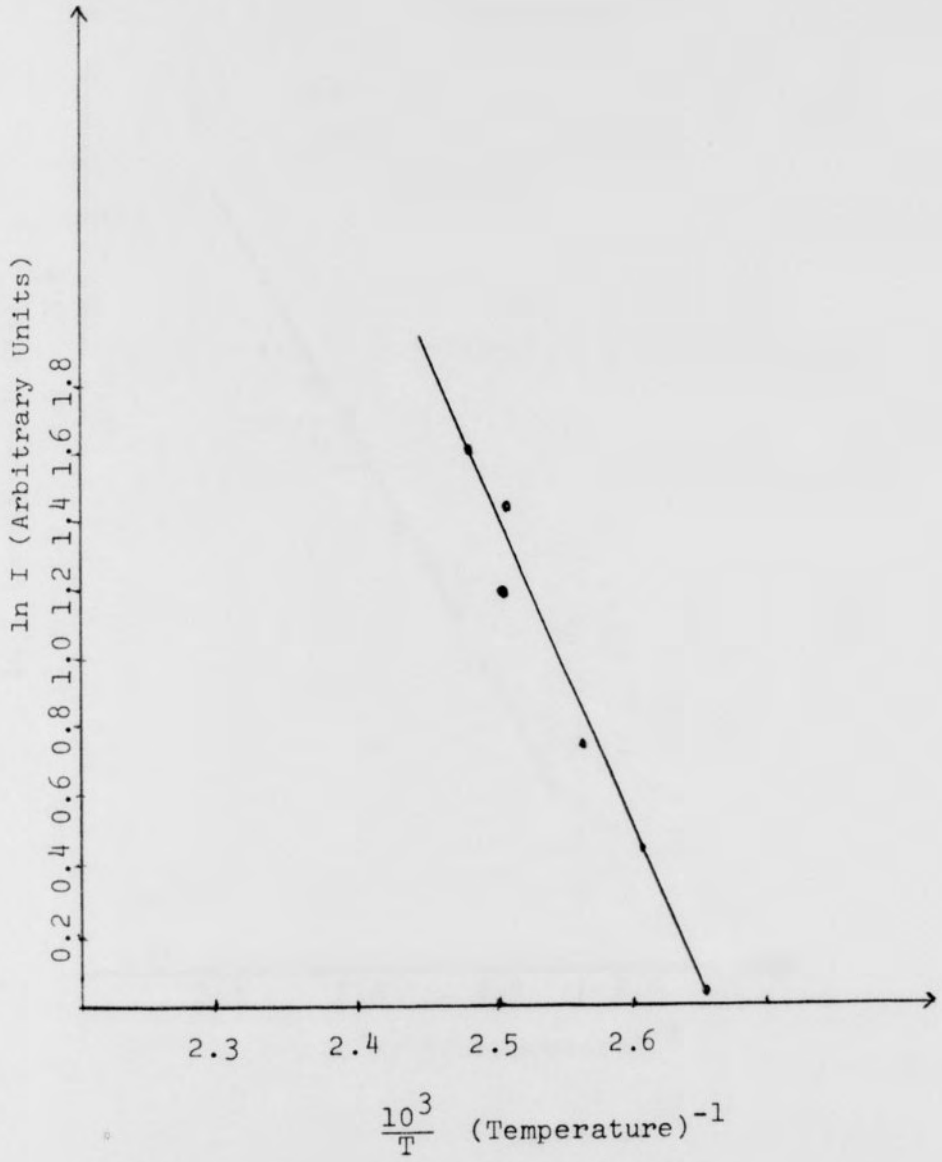

Figure 13

Initial Rise Graph for KBr Crystals

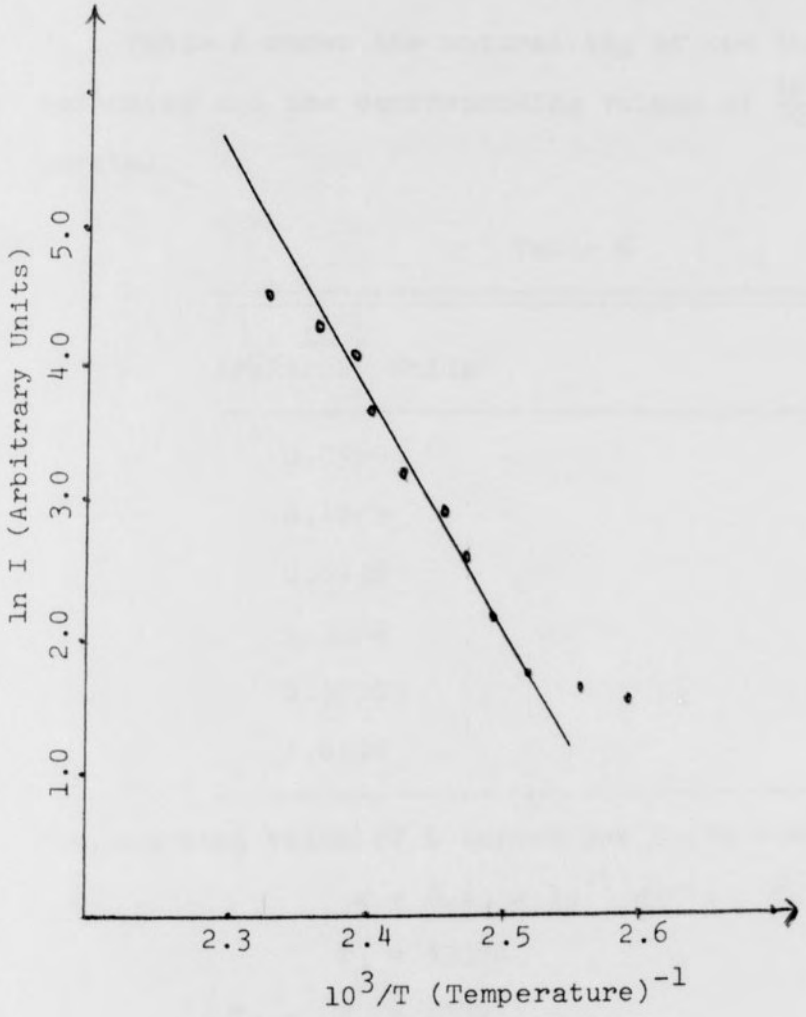

Figure 14

Initial Rise Graph for KCl Crystals

Appendix 2

Table 6 shows the natural log of the thermoluminescence intensity and the corresponding values of $\frac{10^3}{T}$ for KBr crystal.

Table 6

Ln I Arbitrary Units	$10^3/T$ °k-1
0.0960	2.660
0.4050	2.600
0.6930	2.560
1.1300	2.500
1.3900	2.480
1.6100	2.460

The computed value of E turned out to be 0.64 ± 0.04 eV.

$$k = 8.63 \times 10^{-5} \text{ eV/°k}$$

$$T_g = 435°K$$

$$T_2 - T_g = 21°k$$

$$q = 0.775$$

Table 7 shows the natural log of the thermoluminescence intensity and the corresponding values of $\frac{10^3}{T}$ for the KCl crystal.

Table 7

Ln I Arbitrary Units	$10^3/T$ $^\circ k^{-1}$
1.61	2.58
1.62	2.55
1.66	2.52
2.35	2.49
2.62	2.47
2.92	2.45
3.18	2.42
3.50	2.40
3.80	2.38
4.15	2.36
4.47	2.33

The computed value of E turned out to be 1.08 eV ± .02.

$$T_g = 448^\circ k$$

$$T_2 - T_g = 35^\circ k$$

$$q = 2.19$$